Thermochimica Acta, 15 (1976) 55–61

THERMODYNAMIC PROPERTIES OF 3-PENTANOL + DIETHYLAMINE MIXTURES

A. J. G. VAN DIEMEN, C. J. M. HOUTEPEN AND H. N. STEIN
Laboratory of General Chemistry, Technological University, Eindhoven (The Netherlands)
(Received 28 August 1975)

ABSTRACT

Values for excess functions (H^E, V^E, G^E, TS^E) are reported for 3-pentanol + diethylamine mixtures at 298.15 K. The results indicate formation of three hydrogen bonds per molecule 3-pentanol in excess diethylamine, and of two hydrogen bonds per molecule diethylamine in excess 3-pentanol.

INTRODUCTION

Systems containing alcohols and amines are known to exhibit strong hydrogen bond formation[1–4], resulting in strongly negative H^E and TS^E values, and in G^E values which are (in absolute sense) smaller and which may be either positive or negative[5].

In the present investigation, values for excess thermodynamic functions have been obtained for a binary amine + alcohol system not previously studied, consisting of a secondary alcohol (3-pentanol) and a secondary amine (diethylamine) of similar molecular size and shape. The latter factor increases the reliability of some assumptions made in the molecular interpretation of the data.

EXPERIMENTAL

Materials

3-Pentanol, Merck ("Zur Synthese"), was dried on molecular sieve (Union Carbide type 4A) and distilled through a packed column of 1.5 m length at atmospheric pressure. The boiling temperature at 760 Torr* was 388.95–389.15 K (cf. literature[6] value: 388.45 K). Its vapour pressure, measured at 20 different temperatures ranging from 303.30 to 389.00 K could be described by the Antoine equation:

$$\log_{10}(p/\text{Torr}) = 6.7265 - 1014.7/(T/\text{K} - 125.13)$$

The refractive index n_D (293.15 K) was 1.41060 (cf. literature[6] value: 1.4104), the density $d^{298.15}_{277.15}$: 815.40 kg m^{-3} (cf. literature[6] value: 816 kg m^{-3}).

---

*Throughout this paper Torr = (101.325/760) kPa.

Diethylamine, Merck ("Zur Synthese"), was dried on molecular sieve (Union Carbide type 4A), and distilled through a packed 1.5 m length column. The boiling temperature at 760 Torr was 328.45–328.65 K (cf. literature values: 328.48 K[7], 328.60 K[6]). The refractive index n_D (293.15 K) was: 1.38497 (cf. literature[6] value: 1.3864). The density $d_{277.15}^{298.15}$ was: 698.84 kg m^{-3} (cf. literature values: 699.0[7], 701.6[6], 698.93[8]).

n-Heptane, Merck ("Zur Synthese").

2-propanol, the same material as employed previously[9].

Methods

The compositions of liquid mixtures were determined by refractive index.

Excess molar volumes were measured both by means of a pycnometer, and dilatometrically[10]. Both methods were checked by measuring V^E for the system n-hexane + benzene[11,12]; agreement within $\pm 0.01 \cdot 10^{-6}$ m^3 mol^{-1} was obtained.

Excess enthalpies were determined by measuring differential enthalpies of solutions of the pure components in various mixtures by means of an LKB 8700-1 precision microcalorimeter at 298.15 K. Special care was taken to avoid a vapour space in the calorimeter vessel. The instrument was checked by measuring H^E for 2-propanol + benzene mixtures; agreement with data reported by Mrazek and Van Ness[13] and by Brown et al.[14] within ± 15 J mol^{-1} was obtained.

Isobaric liquid–vapour equilibrium was determined in a recirculation still after Raal et al.[15] as described in a previous paper[9].

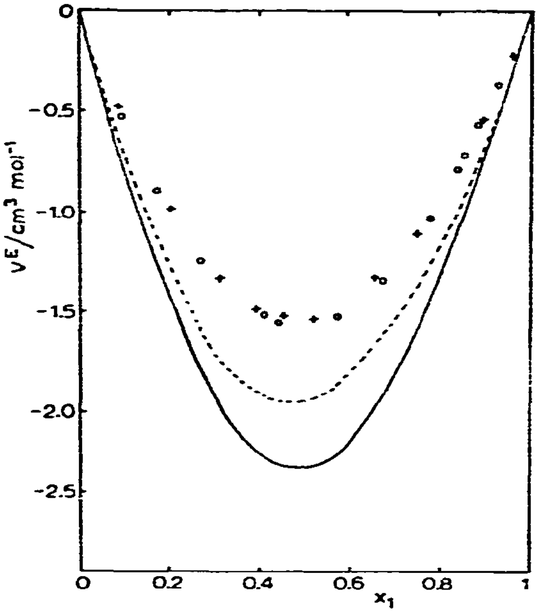
RESULTS

In Fig. 1, V^E vs. x_1 for the systems 2-propanol + diethylamine and 3-pentanol + diethylamine, is compared with V^E for the systems methanol + diethylamine[8] and ethanol + diethylamine[8]. With increasing chain-length of the alcohol, V^E decreases at a given composition, indicating a decreasing tendency for hydrogen bond formation, which is ascribed to sterical screening of the alcohol group by $-CH_3$ and $-C_2H_5$ groups as compared with –H atoms in CH_3OH. The small differences between mixtures containing 2-propanol and 3-pentanol, respectively, at equal molar fraction suggest that increasing the alcohol chain-length beyond that in 2-propanol does not lead to an increased screening of the alcohol group.

Figure 2 shows H^E, G^E and TS^E values. G^E was calculated from LG equilibrium at 760 Torr (Fig. 3) by means of the equations:

$$\ln f_i(298.15\text{ K}; 760\text{ Torr}; x_1) = \ln f_i(T_{eq}; 760\text{ Torr}; x_1) - \\ - \int_{T_{eq}}^{298.15\text{ K}} (H_i(x_1) - h_i)/RT^2 \mathrm{d}T$$

$$G^E = RT \sum_i x_i \ln f_i .$$



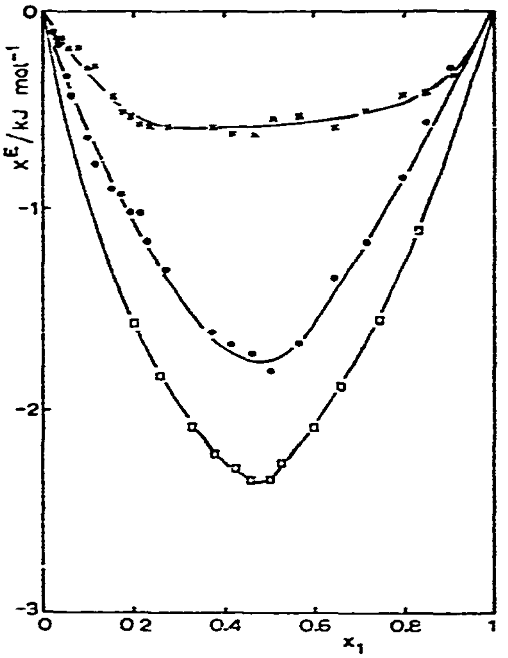


Fig. 1. V^E as function of x_1 at 298 K for the systems: ———, methanol + diethylamine[8]; – – –, ethanol + diethylamine[8]; +, 2-propanol + diethylamine (1); ○, 3-pentanol + diethylamine (1).

Fig. 2. H^E, G^E and TS^E as function of x_B, for the system 3-pentanol + diethylamine (1) at 298 K. ×, G^E; ○, TS^E; □, H^E.

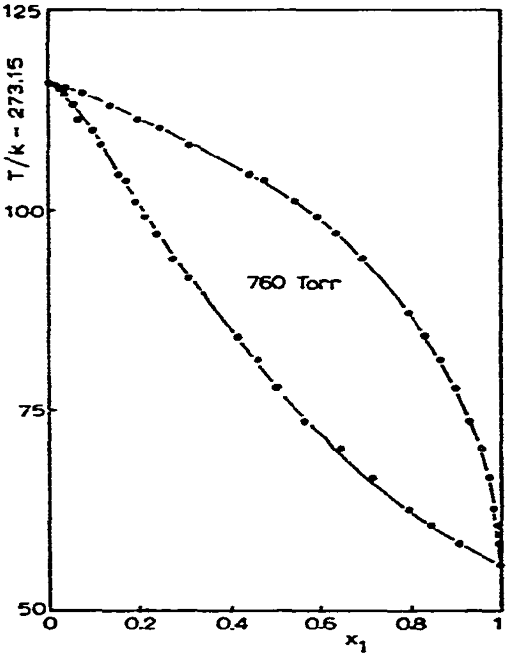


Fig. 3. LG equilibria in the system 3-pentanol + diethylamine at 760 Torr.

TABLE 1

$H_i - h_i$ AND H^E IN MIXTURES DIETHYLAMINE (1)+3-PENTANOL (2)

x_1	$H_1 - h_1$ ($kJ\ mol^{-1}$)	$H_2 - h_2$ ($kJ\ mol^{-1}$)	H^E ($kJ\ mol^{-1}$)
0.000	−10.93	—	—
0.201	−6.21	−0.40	−1.57
0.260	−4.95	−0.73	−1.83
0.297	−4.67	—	—
0.331	−4.10	−1.08	−2.08
0.382	−3.39	−1.50	−2.22
0.427	−2.79	−1.92	−2.29
0.460	−2.44	−2.26	−2.34
0.506	−1.89	−2.81	−2.35
0.527	−1.69	−2.89	−2.26
0.570	−1.28	—	—
0.600	−0.98	−3.76	−2.09
0.659	−0.70	−4.17	−1.88
0.742	−0.37	−4.97	−1.55
0.830	−0.12	−5.87	−1.10
1.000	—	−8.35	—

TABLE 2

ACTIVITY COEFFICIENTS OF DIETHYLAMINE (f_1) AND PENTANOL-3 (f_2) AT 760 Torr LIQUID-VAPOR EQUILIBRIUM CONDITIONS

x_1	f_1	f_2	T_{eq} (K)
0.023	0.310	0.992	388.26
0.032	0.502	0.995	387.71
0.052	0.566	1.003	386.11
0.062	0.683	1.006	384.41
0.112	0.703	1.022	381.16
0.155	0.741	0.981	377.51
0.193	0.792	0.953	374.06
0.212	0.798	0.944	372.16
0.238	0.819	0.939	370.21
0.274	0.839	0.942	367.26
0.373	0.843	0.964	360.16
0.418	0.852	0.947	357.36
0.462	0.868	0.923	354.46
0.507	0.924	0.922	350.81
0.568	0.944	0.867	346.66
0.647	0.945	0.746	343.26
0.716	0.969	0.703	339.61
0.798	0.997	0.558	335.71
0.849	1.011	0.419	333.56
0.907	1.021	0.257	321.26

For these calculations, the vapour pressure of diethylamine at the LG equilibrium temperatures was calculated from Copp and Everett's Antoine equation[16]; deviations from ideal gas behaviour were taken into account for diethylamine (the component with a vapour pressure, at some LG equilibrium temperatures, exceeding 760 Torr) by Hougen et al.'s method[17]. $H_i(x_i)-h_i$, was obtained by interpolation between experimental values (Table 1). The activity coefficients are tabulated in Table 2.

In Table 3 data concerning the differential enthalpies of mixing at low pentanol-3 and low diethylamine concentrations respectively are given. From these data the differential enthalpies of mixing at infinite dilution were extrapolated (see Discussion).

TABLE 3

ENTHALPY CHANGE ON ADDING 3-PENTANOL TO n-HEPTANE

Range of final x (3-pentanol)	*No. of experiments*	*Range of ΔH (kJ per mol 3-pentanol)*
0.0106–0.0125	5	19.50–20.27
0.0026–0.0031	6	21.28–21.80

DISCUSSION

The excess functions are nearly symmetrically arranged around $x = 0.5$, as observed for other binary alcohol+amine systems by Krichevtsov and Komarov[18] and by Nakanishi et al.[5]. As in similar systems[5], $H^E < TS^E < G^E < 0$ at 298.15 K over the whole concentration range. The absolute values of H^E and TS^E in equimolar mixtures, however, are lower than in the cases methanol+diethylamine[5] and ethanol+diethylamine[16], indicating that hydrogen bond formation tendency decreases with increasing alcohol chain-length (cf. the V^E values).

The nearly symmetrical H^E, G^E, TS^E and V^E curves suggest predominant formation of symmetrical, e.g. 1:1, complexes, as found in similar systems by Stevenson[4] from spectroscopic evidence. Lambert and Zeegers-Huyskens[3] assume 1:1 complexes in dilute solutions of alcohols and diethylamine in cyclohexane, although NMR data indicate association of diethylamine with polymolecules of alcohols[19].

It follows from the $H_i - h_i$ values (Table 1) that it is an oversimplification to think of 1:1 complexes, at least at infinite dilution, both of diethylamine in 3-pentanol, and of 3-pentanol in diethylamine. In order to see this, we consider the process of adding isothermally one mol of 3-pentanol to a large amount of diethylamine. The resulting enthalpy change ($H^\infty - h$ for 3-pentanol = -8.35 kJ) may be considered to be composed mainly of 3 parts:

(a) $-\Delta H$ (self association) of 3-pentanol; i.e. the enthalpy change associated with changing OH ... O contacts into non-hydrogen-bonding contacts (e.g., contacts with alkylic $-CH_2$-groups). This quantity was taken to be 22.1 kJ mol^{-1}, found on extrapolating ΔH values for adding small amounts of 3-pentanol to n-heptane

(Table 3) to infinite dilution. This value is of the same order of magnitude as values reported for other alcohols[20–22].

(b) ΔH (network destruction) of the compound present in excess: some bonds between diethylamine molecules will be broken, when hydrogen bonds with alcohol molecules are formed.

(c) ΔH (bond formation).

Other than hydrogen (e.g., dispersion force) bonds are thought to be equal between amine molecules; alcohol molecules; or amine and alcohol molecules. The approximation involved in this assumption is considered to be small compared with the effects of changes in hydrogen bonding (see also ref. 23), especially since the components in the 3-pentanol+diethylamine mixtures have similar molecular sizes and shapes. Then, on adding one mol of 3-pentanol to excess diethylamine, ΔH (bond formation)$+\Delta H$ (network destruction) $= -30.5$ kJ. Since the enthalpy change on formation of one hydrogen bond between an alcohol and diethylamine is known to be -11.0 kJ mol^{-1} (ref. 3) and since ΔH (network destruction) is a positive quantity, it follows that per molecule of 3-pentanol more than one hydrogen bond has to be formed in order to account for the -30.5 kJ mentioned. In fact, the structure of 3-pentanol is compatible with three hydrogen bonds being formed (see Fig. 4a).

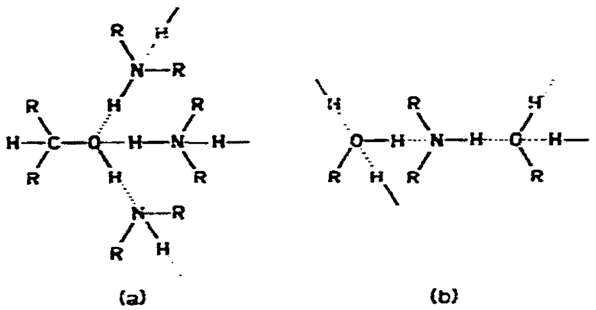


Fig. 4. Hydrogen bond formation possibilities for: (a) 3-pentanol in excess diethylamine; (b) diethylamine in excess 3-pentanol.

A similar calculation for diethylamine in excess 3-pentanol, where $H^{\infty}-h = -10.93$ kJ mol^{-1} and $-\Delta H$ (self association) is estimated to be 8 kJ mol^{-1} by comparison with similar systems,[23,24] results in:

ΔH (bond formation)$+\Delta H$ (network destruction) $= -19$ kJ on adding one mol of diethylamine to excess 3-pentanol. This indicates two hydrogen bonds being formed per diethylamine molecule, as indeed is compatible with the molecular structure (Fig. 4b). These bonds may be directed both towards the same alcohol molecule; this situation might be described as a 1:1 complex. However, when excess alcohol molecules are present, there is no need to assume it; even if it appears, the alcohol molecule concerned will have the possibility to be linked with other alcohol molecules.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the assistance of C. H. C. Fransen in carrying out the V^E measurements.

REFERENCES

1 J. S. Rowlinson, *Liquids and Liquid Mixtures*, Butterworth, London, 2nd ed., 1969, p. 167.
2 H. V. Kehiaian, in A. D. Buckingham and H. A. Skinner (Eds.), *Thermodynamics of Organic Mixtures*, MTP *International Review of Science, Physical Chemistry*, Ser. 1, Vol. 10, *Thermodynamics and Thermochemistry*, Butterworths, University Park Press, 1972.
3 L. Lambert and Th. Zeegers-Huyskens, *J. Chim. Phys.*, 60 (1963) 435.
4 D. P. Stevenson, *J. Am. Chem. Soc.*, 84 (1962) 2849.
5 K. Nakanishi, H. Touhara and N. Watanabe, *Bull. Chem. Soc. Japan*, 43 (1970) 2671.
6 *Selected Values of Properties of Chemical Compounds, TRC Tables*, Vol. I, Texas A & M University, College Station, Texas.
7 T. M. Letcher and J. W. Bayles, *J. Chem. Eng. Data*, 16 (1971) 266.
8 K. Nakanishi and H. Shirai, *Bull. Chem. Soc. Japan*, 43 (1970) 1634.
9 A. J. G. Van Diemen, C. J. M. Houtepen and H. N. Stein, *J. Chem. Thermodyn.*, 6 (1974) 805.
10 W. A. Duncan, J. P. Sheridan and F. L. Swinton, *Trans. Faraday Soc.*, 62 (1966) 1090.
11 R. K. Nigam, B. S. Mahl and P. P. Singh, *J. Chem. Thermodyn.*, 4 (1972) 41.
12 K. R. Harris and P. J. Dunlop, *J. Chem. Thermodyn.*, 2 (1970) 813.
13 R. V. Mrazek and H. C. Van Ness, *A.I. Chem. Eng. J.*, 7 (1961) 190.
14 I. Brown, W. Fock and F. Smith, *J. Chem. Thermodyn.*, 1 (1969) 273.
15 J. D. Raal, R. K. Code and O. A. Best, *J. Chem. Eng. Data*, 17 (1972) 211.
16 J. L. Copp and D. H. Everett, *Disc. Faraday Soc.*, 15 (1953) 174.
17 O. A. Hougen, K. M. Watson and R. A. Ragatz, *Chemical Process Principles*, Vol. II, J. Wiley & Sons, New York, 2nd ed., 1959, Ch. 14, pp. 556–636.
18 B. K. Krichevtsov and V. M. Komarov, *Zh. Prikl. Khim.*, 43 (1970) 703.
19 Th. Zeegers-Huyskens, P. Huyskens and P. Van Tiggelen, *Bull. Soc. Chim. Belge*, 70 (1961) 386.
20 J. E. A. Otterstedt and R. W. Missen, *Trans. Faraday Soc.*, 58 (1962) 879.
21 H. C. Van Ness, C. A. Soczek, G. L. Peloquin and R. L. Machado, *J. Chem. Eng. Data*, 12 (1967) 217.
22 R. M. Stokes and C. Burfitt, *J. Chem. Thermodyn.*, 5 (1973) 623.
23 S. Otin, M. Gracia and C. Gutiérrez Losa, *J. Chim. Phys.*, 70 (1973) 1232.
24 H. Wolff, A. Höpfner and H. E. Höppel, *Ber. Bunsenges. Phys. Chem.*, 71 (1967) 151.